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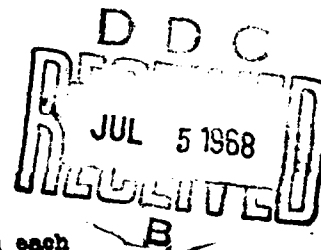
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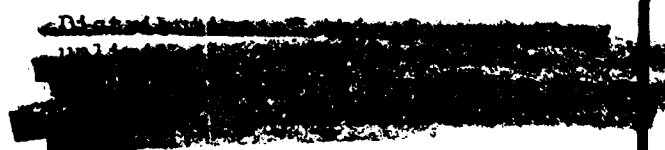
NITROGEN IN METALS
(SELECTED ARTICLES)

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ABSTRACT: The problem of corrosion in reactors for the ammonia synthesis requires selection of materials stable to both hydrogen corrosion and nitration. Alloying of steels with alloying elements that promotes carbides in order to achieve stability against hydrogen, frequently results in dangerous nitriding in the synthesis gas, since most elements promoting carbides simultaneously promote nitriding. At the present time, all problems in this field are solved by corrosion-resistant steels, of which particularly the austenitic steels should be mentioned. They are characterized by suitable formation of the nitride layer, the thickness of which decrease with increasing nickel content in the steel. Stabilized steels with low carbon content also are particularly well suited; of these, steels alloyed with niobium deserve particular mention. It is to be expected that they will lead to a conservation of the expensive steels with higher nickel contents. English translation: 9 pages.

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ABSTRACT : Article discusses certain experimental results on salt-bath nitriding of 30WCrV34.11 hot-forging steel. Purpose of the investigation was to increase the sluicing resistance of injection molds for light alloys by bath-nitriding the hot-forging die steels, which was also to prevent local welding of the light metal to the mold. Aeration of the nitriding bath with compressed air has been shown to be the most favorable and economical process. In this manner, sufficiently thick diffusion zones, combined with the weakest binding zones are obtained in accordance with nitriding time and temperature. Other gases were tried with less satisfactory results. In connection with these experiments attention was also devoted to the individual reaction steps during bath nitriding of hot-forging steels. The probable course of such a reaction is outlined. In conclusion the question as to whether diffusion of the nitrogen into the phase mixture is concluded with simultaneous nitride formation with the alloying elements W, Cr, and V and dissolving of the nitrogen into the ferrite lattice (solid solution formation) is discussed.

English translation: 6 pages.

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THE COMPLEX ACTION OF SYNTHESIS GAS ON ALLOY STEELS
Cr-Mo STEELS AND STAINLESS STEELS

The known hydrogen-resistant Cr-Mo steels for the ranges reported by Nelson (Fig. 1) have also been used previously in the ammonia synthesis. Here the strong nitriding action of the synthesis mixture was not considered [5]. The rapidly advancing nitriding of chrome steels of medium content in contact with the synthesis mixture, limits its application to the range of lower temperatures, 300-350°C. If they are exposed to the synthesis gas, these steels show numerous blisters and cracks at the grain boundaries in the nitride layer, which are typical for hydrogen corrosion.

If it is assumed that some of these steels are sufficiently stable toward hydrogen at about 500°C, it is very probable that the equilibrium between the chromium carbide Cr_7C_3 and the hydrogen is disturbed as a result of nitrogen diffusion and the nitriding of chrome steels of medium content. This results in a shift in the direction of lower stability [6], since chromium forms stable nitrides such as Cr_2N and CrN with nitrogen. As a result, the activity of the chromium in solid solution is reduced, and a thick, brittle nitride layer is formed on the surface of the steel. However, it is not excluded that the cracks are also partially caused by stresses that arise in the embrittled layer during cooling.

Steels whose chromium content lies above the limits of the corrosion-resistant (about 11-12% Cr), behave better. The nitride layers on such steels exposed to synthesis gas are thinner, but very hard and com-

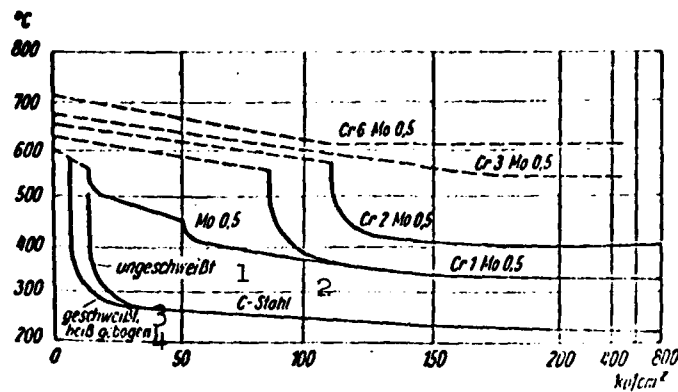


Fig. 1. Working range of carbon steels and alloyed Cr-Mo steels in a hydrogen atmosphere at high pressures and temperatures [3]. 1) Unwelded; 2) C-steel; 3) welded; 4) hot-bent.

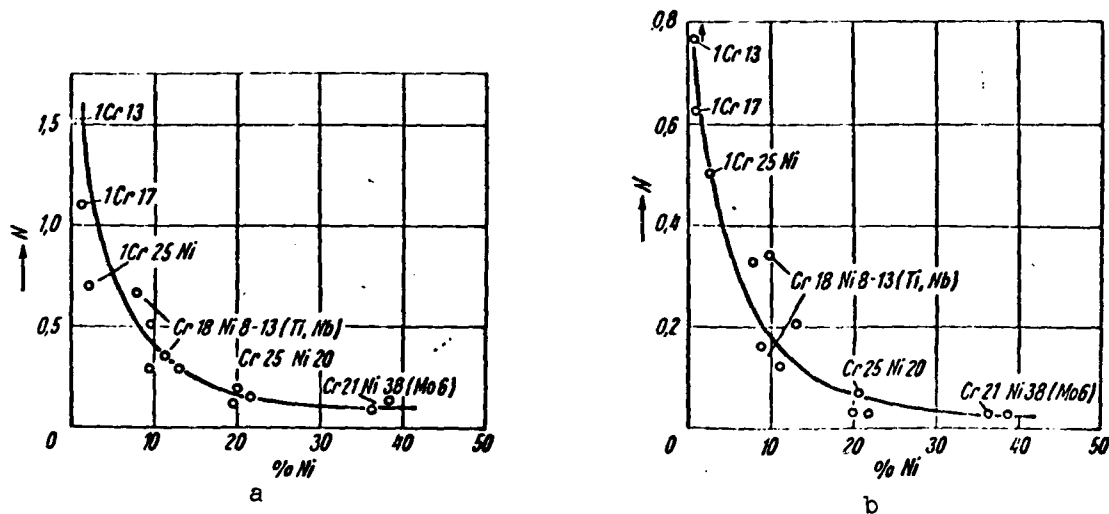


Fig. 2. Influence of nickel content of stainless steels on rate of nitriding (nitrided layer in mm) in the ammonia synthesis. a) At high pressure (900 kp/cm^2); b) at medium pressure (325 kp/cm^2).

pact, and mostly without cracks; this can be explained by the higher stability of the Cr_{23}C_6 carbides which are present. The layer thickness increases gradually, and the cracks occur only sporadically, as a result of severe stresses in this layer. The austenitic corrosion-resistant steels are considered to be best suited for the internal equipment of reactors for the ammonia synthesis. The nitriding rates of these

steels are low and appear to depend more on the nickel content than on the chromium content; this has been confirmed by experiments on several types of steel that had been exposed to high-pressure or medium-pressure synthesis (Fig. 2a, b). The effort to conserve nickel gave impetus to work with steels without a nickel content, which should be extremely resistant against the action of hydrogen and any possible nitriding. These steels will be discussed below.

W-Ti AND Ni-Ti STEELS

Allowing for the influence of nitrogen and nitriding on the reduction of the activity of chromium in Cr-Mo steels, strong carbide-promoting elements should be preferred as alloying elements. Only the elements titanium and niobium deserve special consideration for increasing the stability of carbon steels against hydrogen. Due to the strong bonding of carbon to titanium and niobium, stabilized steels resist the destructive action of the synthesis gas.

Even with the lower activity of titanium, the stability of these carbides is sufficient to prevent, on the one hand, the penetration of atomic nitrogen and, on the other, the liberation of carbon. This is in contrast to steels of a medium Cr content. Action of hydrogen can be established with these steels only at a low content (theoretically in a ratio which is not stoichiometric) of the stabilizing element, i.e., if cementite is present in the structure.

The first experiments relative to increasing the stability of steels stabilized only with titanium, which, in addition, were alloyed with tungsten and nickel, showed that although they are stable against hydrogen corrosion, they are not against nitriding, which varied in extent and caused serious embrittlement of the surface.

If the thicknesses of the nitrified layer are compared to the curve of its hardness in dependence on the contents of carbon, titanium, niob-

ium, tungsten and nickel in steels, certain conclusions regarding the influence of these elements on the sensitivity to nitriding can be drawn.

Of great interest is the influence of the free content of titanium on the ratio of titanium to carbon as related to the intensity of nitriding, which is shown in Fig. 3. With a stoichiometric excess content of titanium to the carbon, a rapid increase in the nitrided-layer thickness and hardness is obtained; its maximum lies approximately at a ratio $Ti:C = 9:1$. With none of the stabilized steels investigated was hydrogen

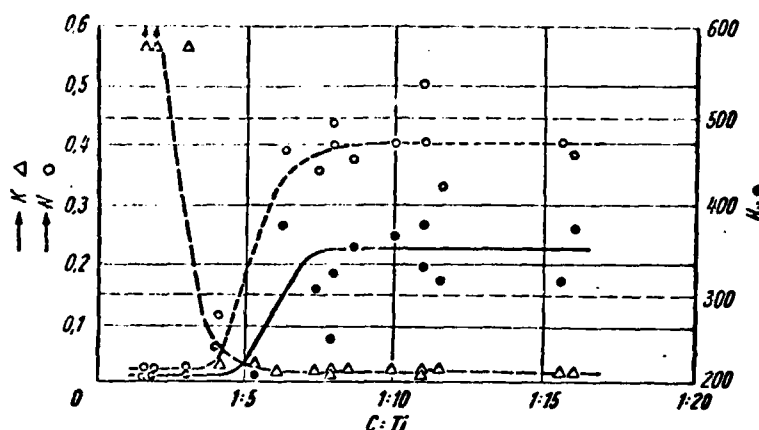


Fig. 3. Influence of the Ti:C ratio in W-Ti and Ni-Ti steels on tendency to nitriding (thickness N in mm and hardness H_v in kp/mm^2 of the nitrided layer) and to hydrogen corrosion (depth of penetration of hydrogen corrosion K in mm). Synthesis gas pressure 900 kp/cm^2 , temperature 500°C , duration of experiment 500 hours.

corrosion or cracking observed in the layer. Tungsten up to 4.5% appears to have no influence on the thickness of the nitride layer (Fig. 4). The hardness of the layer increases at about 4% tungsten. Nickel does not have a substantial influence on either the thickness or the hardness of the nitrided layer. At a nickel content of 3%, the thickness of the nitride layer becomes slightly smaller.

With regard to inhibiting nitriding of steels stabilized with ti-

tanium, the following points should be noted:

- a) Lowering the titanium content to or below stoichiometric Ti:C ratio with the simultaneous presence of tungsten in the steel.
- b) Testing of steels stabilized with niobium regarding their tendency to nitriding and hydrogen corrosion.
- c) Surface protection of steels against nitriding by means of copper plating or nonelectrolytic nickel plating.

Increasing the titanium content, in order to increase strength at higher temperatures, in steels with tungsten contents up to 4% minimizes hydrogen corrosion at a temperature of 500°C; here the Ti:C ratio lies between 4 and 4.5:1 (Fig. 3). This ratio depends on the content of nitrogen and oxygen in the steel, on grain size, etc. At lower temperatures (for example, 420°C), the steel is stable against hydrogen corrosion up to a certain hypostoichiometric Ti:C ratio of about 3:1 with 1.5% W, with no nitriding by the synthesis gas.

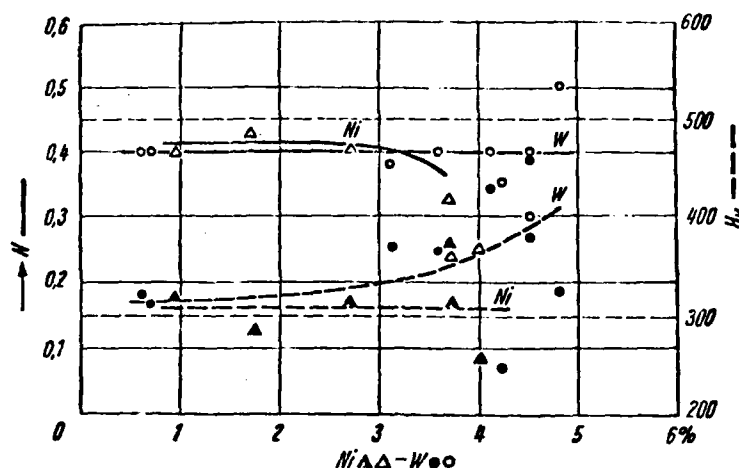


Fig. 4. Influence of tungsten and nickel on thickness (N in mm) and hardness (H_v in kp/mm^2) of nitrided layer on W-Ti and Ni-Ti steels (experimental conditions as in Fig. 3).

In view of all the above experience, it is necessary that for the highest temperatures in the ammonia synthesis, the W-Ti or Ni-Ti steel

should have a content of titanium at which all the carbon in the steel is bound to a stable carbide, without the presence of free titanium in solid solution. This requirement limits practical application of this type of steel at the highest temperatures, since major metallurgical difficulties arise. Consequently, it is more suitable to use these steels at lower temperatures (at about 420°C) for gas-gas heat exchangers in the reactor for the ammonia synthesis. For this application, it is possible to use a broader Ti:C ratio in the steel at a reduced W content of 1.5%.

With regard to limitation of the nitriding effect on steels stabilized with titanium, the surface was nickel-plated without current or electrolytically copper-plated. Both layers are well suited for the prevention of nitrogen diffusion in the material. They are without influence on the rate of hydrogen corrosion in unalloyed carbon steels. The hydrogen penetrates the layers and forms numerous blisters on the coatings; this makes our process appear unsuitable for industrial use.

STEEL STABILIZED WITH NIOBIUM

Steels stabilized with niobium, in contrast to steels alloyed with titanium, do not have a tendency to nitriding, even if the Nb:C ratio exceeds 10:1 (Fig. 5). This eliminates the deficiencies arising with steels stabilized with titanium.

The use of niobium in these steels does not require strict adherence to the upper limit of niobium content with regard to nitriding. A less-than-stoichiometric content of niobium in these steels (steels free of other elements were investigated) results in strong hydrogen corrosion, as in steel alloyed with titanium and having cementite in its structure. The smaller increase in the hardness on the surface as compared to steels stabilized with titanium indicates the advantages of steels stabilized with niobium.

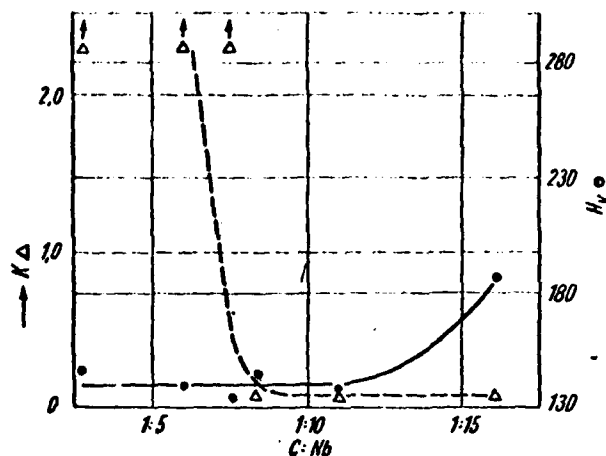


Fig. 5. Influence of Nb:C ratio in steels stabilized with niobium on nitriding, presented in hardness units of H_V kp/mm^2 , and on hydrogen corrosion (K in mm). The experimental conditions are as in Figs. 3 and 4. The thickness of the nitrided layer could not be determined satisfactorily as a result of the small hardness difference between the layer and the core.

CONCLUSIONS

The problem of corrosion in reactors for the ammonia synthesis requires selection of materials that are stable to both hydrogen corrosion and nitration. Alloying of steels with alloying elements that promote carbides in order to achieve stability against hydrogen, frequently results in dangerous nitriding in the synthesis gas, since most elements promoting carbides simultaneously promote nitriding.

At the present time, all problems in this field are solved by corrosion-resistant steels, of which particularly the austenitic steels should be mentioned. They are characterized by suitable formation of the nitride layer, the thickness of which decreases with increasing nickel content in the steel. Stabilized steels with low carbon content also are particularly well suited; of these, steels alloyed with niobium deserve particular mention. It is to be expected that they will lead to a conservation of the expensive steels with higher nickel contents.

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Discussion

of Paper Presented by Dr. Felgel-Farnholz

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(FE Laboratory for Materials, VEB Carl Zeiss):

SOME OBSERVATIONS ON SALT BATH NITRIDING OF HOT-FORGING STEEL

Following the interesting statements by Dr. Felgel-Farnholz on gas and bath nitriding of structural, nitriding and cold-forging steels, certain experimental results on salt-bath nitriding of 30WCrV34.11 hot-forging steel should be made known.

The purpose of the investigations was to increase the sluicing resistance of injection molds for light alloys by bath-nitriding the hot-forging die steels, which was also to prevent local welding of the light metal to the mold. The first experiments indicated that in order to attain the surface quality demanded by CZ for injection-molded parts, the binding zone must definitely be machined off after bath nitriding of the mold parts, since, due to its brittleness and the temperature changes occurring continually in use (thermal-mechanical stress cycles) it cracks off and a pockmarked surface is formed. After it had been confirmed by endurance tests that the diffusion zone that follows the binding zone meets the requirements mentioned above, the problem was to regulate the nitriding process in such a manner that with the thinnest possible binding zone, sufficiently strong diffusion zones would be obtained so that machining off the binding zones would remain within economically feasible limits.

Aeration of the nitriding bath with compressed air has been shown to be the most favorable and economical process. In this manner, sufficiently thick diffusion zones, combined with the weakest binding zones are obtained in accordance with nitriding time and temperature.

Figure 1 compares curves of micro-hardness in the diffusion zones versus depth of penetration for constant nitriding conditions with non-aerated and aerated baths for 30WCrV34.11 hot-forging steel. For the ordinate $H_m = 600 \text{ kp/mm}^2$, which is established as the limiting value, the depths of penetration E_1 and E_2 are obtained as values of the abscissa.

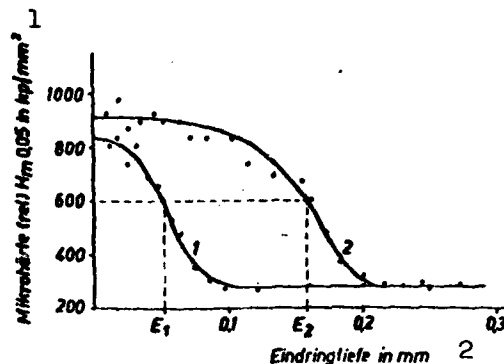


Fig. 1. 30WCrV34.11 as supplied (280 HV 10). Bath nitriding 240 min. 1) Without aeration; 2) aeration 15 liters/hr; $V_{\text{bath}} = 1960 \text{ cm}^3$. 1) Micro-hardness (rel) H_m 0.05 in kp/mm^2 ; 2) depth of penetration in mm.

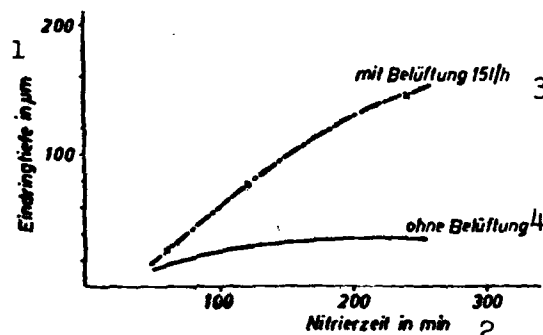


Fig. 2. Curve of depth of nitriding in dependence on time, on the basis of $H_m(\text{rel}) = 600 \text{ kp/mm}^2$ ($p = 50 \text{ p}$) for 30WCrV34.11 as delivered. 1) Depth of penetration in μ ; 2) nitriding time in min; 3) with aeration, 15 liters/hour; 4) without aeration.

The aeration of the bath deepens the diffusion zone by more than 0.1 mm. It now amounts to 0.158 mm, as compared to 0.052 for nitriding

treatment without bath aeration. Figure 2 shows the advantage of bath aeration in a representation of the microhardness curve in the diffusion zone in dependence on the nitriding time. With nitration times between 100 and 200 minutes, the depths of diffusion are increased 2- to 3-fold. By systematic variation of the variables (nitriding time and temperature), nitrided zones with the thinnest binding layers and maximum diffusion zone depth were obtained with aeration (binding zone 5-8 μ , diffusion zone up to $H_m = 600 \text{ kp/mm}^2$ approximately 120 μ). The acceleration of the nitriding process can best be recognized in the hot-forging steels for short-time nitriding treatment and low temperature. Figure 3 summarizes the microhardness curves in dependence on time for the nitriding condition 500°C/30 min. The compressed-air flow rate is the parameter. An increasing rate of air flow results in better nitriding. Particularly noticeable is the accelerating action for aeration

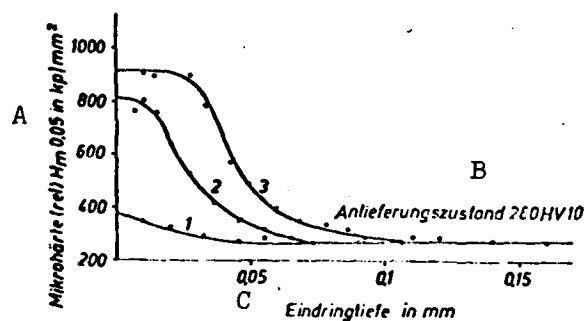


Fig. 3. 30WCrV34.11 - Bath nitriding 500°C; 30 min. 1) Without aeration; 2) aeration, 25 liters/hour, $V_{\text{bath}} = 1960 \text{ cm}^3$. A) Microhardness (rel) H_m 0.05 in kp/mm^2 ; B) material as delivered, 280 HV 10; C) depth of penetration in mm.

with 25 liters/hour. While no diffusion zone capable of functioning is present with normal nitriding treatment, it amounts to 0.022 and 0.043 mm with aeration. These positive results were not obtained in experiments with other gases. Thus, on aeration with pure nitrogen, only an insignificant increase in the diffusion zone was established, which, as

was shown by parallel experiments with mechanical bath agitation, is of the same order of magnitude as the improvement by convection. The activation of the nitriding process can consequently be traced solely to the action of oxidizing gases.

In connection with these experimental results, we became interested in the individual reaction steps during bath nitriding of hot-forging steels. An attempt was made to represent the individual reactions schematically step by step. Accordingly, the following course of reaction is probable (Fig. 4):

- 1) Thermal dissociations of the sodium cyanide and potassium cyanate; cleavage of the cyanide and cyanate groups.
- 2) Adsorption of the nitrogen atoms on the surface of the sample.
- 3) Dissolving of the atomic nitrogen into the phase mixture with the following steps: nitride formation with the alloying elements chromium, tungsten and vanadium (segregated-nitride formation) and dissolving of the nitrogen in the α -Fe-unit cell (formation of solid solution).

The extent to which catalytic processes influence nitriding has not been determined up to the present time.

Thermal dissociation and cleavage of the cyanide and cyanate groups can be considered as the factors which determine the rate of the nitriding process, while adsorption of N-atoms on the metal surface and the diffusion of nitrogen into the phase mixture itself probably do not determine rate. This can be stated with certainty for diffusion, on the basis of calculations of activation energy with the aid of the Arrhenius equation, since the same activation energy of $Q = 30,600$ cal/mole is found with and without bath aeration. The acceleration of the nitriding process can consequently probably be attributed only to activation of thermal dissociation and cleavage of the radicals under the influence of oxygen.

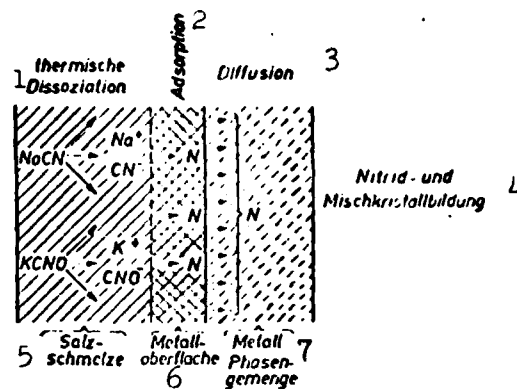


Fig. 4. Diagram of the reaction steps possible during bath nitriding of hot-forging steel. 1) Thermal dissociation; 2) adsorption; 3) diffusion; 4) nitride and solid solution formation; 5) salt melt; 6) metal surface; 7) metal phase mixture.

Also of interest is the question as to whether diffusion of the nitrogen into the phase mixture is concluded with simultaneous nitride formation with the alloying elements W, Cr and V and dissolving of the nitrogen into the ferrite lattice (solid solution formation). According to our previous investigations, both processes take place side by side. However, the primary process, which also causes the enormous increase of hardness in the outermost boundary zones, is the formation of a state of residual stress of the first kind, with residual compressive stress in the surface layers, by segregated-nitride formation. Even though X-ray diffraction measurements and dilatometric tests indicate an additional intercalation of atomic nitrogen into the ferrite lattice, these observations have to be evaluated extremely critically for two reasons. Firstly, it can be expected that, for example, W, Cr and V, which are intercalated substitutionally in the α -crystal, limit the nitrogen concentration in the ferrite until all their atoms are bound with nitrogen. If all W, V and Cr atoms have been bound out as nitrides, it can be assumed that the residual compressive stresses in the surface of the sample would become so great that the solubility of the nitrogen

would be greatly reduced and its diffusion hindered.